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Chemically modified multiwalled carbon nanotubes as efficient and selective sorbent for separation and preconcentration of trace amount of Co(II), Cd(II), Pb(II), and Pd(II)



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Abstract Multi-walled carbon nanotubes (MWCNTs) were chemically functionalized by glutaric dihydrazide (GDH) and characterized with FT-IR technique. This new sorbent was used for enrichment and preconcentration of Co(II), Cd(II), Pb(II), and Pd(II) ions. The adsorption was achieved quantitatively on MWCNTs at pH 4.0, and then the retained metal ions on the adsorbent were eluted with 1.5 mol L⁻¹ HNO₃. The effects of analytical parameters including pH of the solution, eluent type, sample volume, and matrix ions were investigated for optimization of the presented procedure. The adsorption capacity of the adsorbent at optimum conditions was found to be 33.6, 29.2, 22.1, and 36.0 mg g⁻¹ for Co(II), Cd(II), Pb(II), and Pd(II), respectively. The LOD values of the method were 0.16, 0.19, 0.17, and 0.12 ng mL⁻¹ (3Sb, *n* = 10) for Co(II), Cd(II), Pb(II), and Pd(II), respectively. The RSDs values of the method were 0.75, 0.85, 1.16, and 1.30 ng mL⁻¹ for Co(II), Cd(II), Pb(II), and Pd(II), respectively. The method was applied for the determination of analytes in soil, well water, and wastewater samples with satisfactory results.

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1. Introduction

Heavy metals, in environment and biological fluids are one of the major sources of pollution. Small amounts of these elements are common in our environment and actually necessary for good health but large amounts of them may cause acute and chronic toxicity. Because of these reasons the determination of metal ion concentrations in environmental samples is one of the most important fields of the analytical chemistry

(Han et al., 2011; Zhang et al., 2012; Mashhadizadeh and Karami, 2011). Therefore, control and accurate determination of trace metals in environment and biological fluids is of paramount importance (Parinejad et al., 2008). The common availability of the instrumentation, simplicity of the procedures, speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternative (Yang and Fan, 2008; Vagheti et al., 2009). Monitoring of trace element concentrations in biological materials, particularly biological fluids, might be considered a difficult analytical task, mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a preconcentration step (Ghaedi et al., 2007). The determination of trace metals by flame atomic absorption spectrometry (FAAS) has a number of advantages such as high selectivity, speed and fairly low operational cost. Despite of its significant analytical and chemical capacities for metal determination at low concentration levels, FAAS often requires a suitable pretreatment step of the sample in order to facilitate the desired sensitivity and selectivity of the measurement (Mashhadizadeh et al., 2003). For these reasons, an efficient separation and preconcentration procedure is often required prior to the measurement step (Chen et al., 2009). Solid phase extraction (SPE) is a prevalent technique for separation and preconcentration of metal ions in environmental samples, due to its simplicity, rapidity, minimal cost, low consumption of reagents and the ability of combination with different detection techniques in the form of on-line or off-line mode (Fritz, 1999; Behbahani et al., 2014a,b; Nabid et al., 2012).

Solid phase extraction has several advantages over other separation techniques in view of: (i) trace and major concentrations of trace ions present in hazardous samples can be removed with equal ease; (ii) higher enrichment factors; (iii) reusability of the adsorbent; (iv) absence of emulsion; (v) minimal costs due to low consumption of reagents; (vi) ease of automation; (vii) environmental friendly; (viii) safety with respect to hazardous samples. Accordingly, several solid phase extractants have been employed for enrichment of traces of elements from dilute solutions (Poole, 2003; Dean, 1998; Behbahani et al., 2014a,b; Nabid et al., 2011). In this respect, SPE has commonly been used as a selective technique for preconcentration/separation of various inorganic species and enhanced selectivity is achieved because of the discriminatory binding of the analyte to a solid support and accumulated analyte is subsequently eluted with a small volume of solvent. The adsorbents with high surface area are preferred in solid phase extraction of traces of heavy metals.

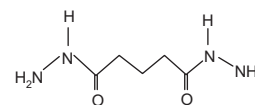
Several adsorbents have been studied for the adsorption of the metal ions such as activated carbon, alumina-coated magnetite nanoparticles, fly ash, activated sludge, zeolite, rice husk, alumina, silica gel, resins, etc. (Tavallali et al., 2013; Ghaedi et al., 2009; Adams et al., 2009; Al-Degs et al., 2008; Chai et al., 2010). However, these adsorbents suffer from low adsorption capacities or removal efficiencies of metal ions. Therefore, researchers have carried out investigations for new promising adsorbents.

In recent years, a great attention on the application of nano-structure materials, especially carbon nanotubes (CNTs) is remarkable. Particularly, there have been an increasing number of applications of CNTs in several fields of chemical analysis (Ding et al., 2008). CNTs can be visualized as a sheet of

graphite rolled into a tube. These tubes are classified as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the carbon atom layers in the wall of the nanotubes (Iijima and Ichihashi, 1993). Because of their special electronic, metallic and structural characteristics as well as the unique tubular structures of nano diameter and large length/diameter ratio (Grobert, 2007), CNTs have been exploited in analytical chemistry and other fields (Tan et al., 2008; Al-Degs et al., 2009; Ding et al., 2006).

The change in nature of surface CNTs by suitable materials generally improves selectivity and sensitivity of the determinations (Wang et al., 2009); therefore important to develop adsorbent material that can perform the function via two mechanisms simultaneously which are chemisorptions and physisorption. Physisorption is the interaction when an atom or molecule is bound to the surface of a solid by van der Waals forces. On the other hand, chemisorption involves stronger forces and forms chemical bonds that involve the transfer or sharing of electrons. This occurs when an atom or molecule is bound to a surface through overlapping of one or more of its electron orbitals (Clark, 1974). Chemical modifications of CNT surfaces have been a key research area due to their hydrophobicity properties in aqueous systems. Surface functionalization can effectively improve the dispersibility and reactivity of the CNTs for application in aqueous systems (Mansor et al., 2012); therefore CNTs may be used for separation and preconcentration metal ions from different matrixes. (Soylak et al., 2008; Afzali and Mostafavi, 2008; Fang et al., 2007; Huang et al., 2009).

However, the adsorption capacity of the raw or oxidized-MWCNTs for SPE is quite limited, especially for metal ions (Zang et al., 2009). According to our literature survey, until now, there were no references to the application of glutaric dihydrazide (GDH)-modified MWCNTs for simultaneous separation and preconcentration of trace amounts of metal ions. Ligand structure of glutaric dihydrazide is shown in Scheme 1. MWCNTs modified with some organic compounds are expected to be more selective than untreated and oxidized-MWCNTs for the solid phase extraction of metal ions. In this study, we report the synthesis, characterization and application of glutaric dihydrazide modified multiwalled carbon nanotubes (MWCNTs-GDH) as a selective sorbent in SPE for separation and preconcentration of Co(II), Cd(II), Pb(II), and Pd(II) prior to their FAAS determination. The main reason for using glutaric dihydrazide as a modifier for MWCNTs was that GDH is a good source of electrons that causes an increasing in adsorption capacity. The new adsorbent of MWCNTs-GDH has a high adsorption capacity for SPE of studied metal ions present in the soil, well water and wastewater samples. The analytical conditions for the preconcentration (quantitative retentions) of analyte elements were investigated. Most of the previously reported MWCNTs modified in view of their advantage suffer from limitation such as high detection



Scheme 1 Ligand structure of glutaric dihydrazide.

limit (Table 1). In our sense, this limitation can be overcome by simultaneous incorporation of nanoparticles and chemical immobilization of carbon surface. The developed method is simple, rapid, precise, accurate and reliable offering a higher preconcentration factor and adsorption capacity for the above metal ions rather than other sorbents.

2. Experimental

2.1. Apparatus

A Model Sens AA atomic absorption spectrometer (GBC Scientific Equipment USA LLC, Hampshire, IL) equipped with a deuterium background corrector and with Co, Cd, Pb, and Pd hollow-cathode lamps as radiation sources was used for absorbance measurements. All measurements were carried out in an air/acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations. The functional groups on the surface sites of adsorbents were detected by an FTIR spectrometer (Model FT/IR 400 type A, JASCO, Tokyo, Japan) using KBr pellets. A digital pH meter (Jenway Model 3510) equipped with a combination glass-calomel electrode was used for pH adjustment which calibrated against two standard buffer solutions at pH 4.0 and 10.0 was used to measure the pH of the solutions.

2.2. Chemicals and reagents

Chemicals used for the preparation of all standard and sample solutions were from Merck (Darmstadt, Germany). Deionized water was used for all dilutions. In order to avoid contamination, laboratory glassware was repeatedly cleaned by a 10% (v/v) HNO₃ solution and rinsed with deionized water prior to use. The 1000 mg L⁻¹ standard solutions of the studied elements were supplied by Merck. The working solutions of metals were prepared by series dilution of their stock solutions immediately prior to use. Universal aqueous pH buffer solutions were

formulated from acetic/phosphoric/boric acids (0.04 mol L⁻¹ each) and adjustments of the desired pH were made with HCl and NaOH (1.0 mol L⁻¹). MWCNTs used in the experiment were bought from the Research Institute of Petroleum of Iran RIPI (Tehran, Iran). The length of MWCNTs was in the range of 10–50 µm, and outer diameter in the range of 10–30 nm. The special surface area and thermal conductivity of the MWCNTs were 270 m² g⁻¹ and 1500 W/mK (watt/meter-Kelvin), respectively. The GDH ligand was synthesized according to the literature (Hajipour et al., 2007). Used automobile catalyst pellets (standard reference material 2556) were purchased from NIST. Pb, and Cd were used as the stock standards for preparing the working standards (Part Nos. Pb: N9300128; Cd: N9300107). Certified reference materials: spinach leaves NIST 1570a (National Institute of Standards and Technology, Gaithersburg, USA) were analyzed.

2.3. Synthesis

2.3.1. Synthesis of the carboxylic derivative of MWCNTs (MWCNTs-COOH)

Raw MWCNTs were heated at 300 °C for 1 h to remove amorphous carbon, and then purified with HCl (10%) to remove the metal ions and other impurities adsorbed on them. Prior to use, MWCNTs were oxidized with concentrated HNO₃ to create binding sites on the surface of the MWCNTs. For the oxidation, 3.0 g of MWCNTs was suspended in 100 mL concentrated HNO₃, and then refluxed for 20 h at 120 °C with vigorous stirring. Afterward, the oxidized MWCNTs were washed with deionized water to remove any excess nitric acid and reach neutral pH, and then dried in an oven at 80 °C for 8 h.

2.3.2. Synthesis of MWCNTs-GDH

A 2.0 g amount of MWCNTs-COOH produced in the previous step was suspended in an appropriate amount of thionyl chloride (SOCl₂) and 1.0 mL dimethylformamide, and then

Table 1 Comparative data from some recent studies on preconcentration.

Analyte	Matrix	MWCNTs characteristics	LOD ^a	Remarks	Reference
Co	Tap and river water	o.d: 10–30 nm, length: 5–15 µm	0.55 µg L ⁻¹	MWCNTs were oxidized with HNO ₃	Afzali and Mostafavi (2008)
Cr, Fe, Pb	Yellow River water and biological samples	o.d: 15–65 nm, length: 10–50 µm	0.24, 0.19, and 0.33 ng mL ⁻¹ for Cr, Fe and Pb, respectively	MWCNTs were modified with ethylenediamine	Zang et al. (2009)
Au, Mn	Wastewater, tap and well water	length: 1–10 µm Purity: 95%	0.01 and 0.03 ng mL ⁻¹	MWCNTs were modified with NBHAE	Shamspur (2009)
Cu, Cd, Pb, Zn, Ni, Co	Apple leaves and wheat gluten	Surface area and density of MWCNTs: 600 m ² g ⁻¹ and 2.1 g mL ⁻¹	0.30–0.60 µg L ⁻¹	MWCNTs/APDC	Tuzen et al. (2008)
Co, Cd, Pb, Pd	Waste water, well water, and soil	MWCNTs: od: 10–30 nm, length: 10–50 µm	0.16, 0.19, 0.17, and 0.12 µg L ⁻¹ for Co, Cd, Pb and Pd respectively	MWCNTs were modified with GDH	Present work

^a Detection limit.

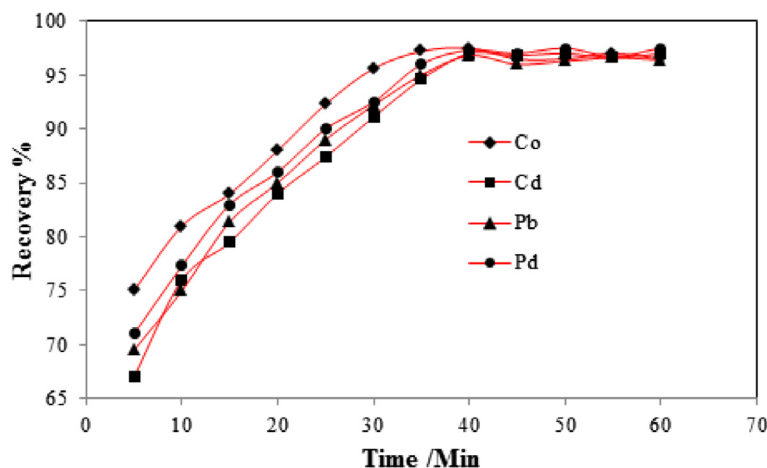


Figure 1 Effect of time the mixture was shaken vigorously to facilitate the adsorption of the metal ions onto the adsorbent.

refluxed for 13 h at 70 °C with stirring. The result was MWCNTs-SOCl. Afterward, we removed any excess SOCl₂ by distilling the mixture. In the last step, the waterless product was mixed with 1.2 g GDH in 100 mL cyclohexane and stirred for 8 h at 80 °C (Abdel Salam and Burk, 2008). After centrifugation, the black solid was washed with deionized water until the wash water was clear. The remaining black solid was retained after drying at 60 °C in an oven.

2.4. Batch method

A batch method was used for efficient adsorption of analytes onto MWCNTs-GDH for all of the studies in this work. A series of sample solutions containing Co(II), Cd(II), Pb(II), and Pd(II) ions was transferred to and diluted in a 250 mL flask, after adjusting the pH to the desired value with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH, and adding suitable buffer solutions. A 250 mg amount of MWCNTs-GDH was added, and the mixture shaken vigorously for 40 min to facilitate the adsorption of the metal ions onto the adsorbent (Fig. 1).

It was then filtered. The retained MWCNTs-GDH were washed with 4 mL 1.5 mol L⁻¹ HNO₃, and the concentrations of the metal ions were directly determined by FAAS.

2.5. Pretreatment of real samples

The soil sample was digested as follows: 40 g soil sample was put in a beaker, and 20 mL distilled deionized water, 24 mL HNO₃, and 6 mL H₂O₂ (30%) were added. The mixture was stirred and heated on a hot plate until it decreased to half of its initial volume; it was then filtered and diluted in a 200 mL volumetric flask with distilled water.

Well water and wastewater samples were collected from husbandry well Zarand Kerman, Iran and Sarchashmeh of Kerman Industrial State, Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (EMD Millipore, Billerica, MA) with a pore size of 0.45 µm. The organic content of the water samples was oxidized in the presence of 1% H₂O₂ (30%) by addition of concentrated nitric acid. The water samples were filtered through a filter paper after

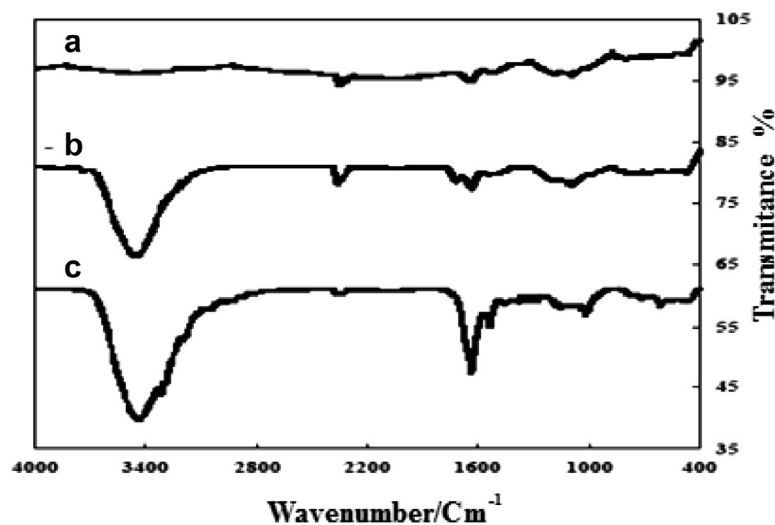


Figure 2 FTIR spectra of (a) MWCNTs, (b) oxidized MWCNTs, and (c) MWCNTs-GDH.

acidification to 1% with concentrated nitric acid; they were stored in polyethylene bottles (Ghaedi et al., 2007). Soil and water samples were collected in June 2013.

3. Results and discussion

In this study, one-variable-at-a-time optimization approach was used for the optimization of separation conditions. The parameters affecting the performance of the extraction were investigated. When one parameter changed, the other parameters were fixed at their optimized values.

3.1. Characterization of the chemically modified MWCNTs with FTIR spectrometry

FTIR spectrometry measurements were performed to provide more evidence of attachment of GDH to the MWCNTs. Fig. 2 shows the IR spectra of the raw MWCNTs, oxidized MWCNTs, and MWCNTs-GDH. Comparison of the FTIR spectra of MWCNTs-COOH with MWCNTs showed the appearance of a new band (1709 cm^{-1}) in MWCNTs-COOH due to the C=O stretching vibration of the COOH group,

which indicated that the carboxylic derivative of MWCNTs was prepared successfully. When MWCNTs-COOH was modified by GDH, several new peaks appeared in the spectrum. According to the literature (Pretsch et al., 2009), the new peaks can be assigned as follows: The peak at 1528 cm^{-1} was caused by a C–N stretching vibration and N–H bending vibration, and the bands around 3312 cm^{-1} were caused by an NH_2 stretching vibration.

3.2. Effect of the sample pH

As pH of the sample solutions is one of the most important analytical factors in the adsorption of metal ions onto MWCNTs-GDH, the effect of pH on the recovery of analyte ions was determined in the pH range 1.0–9.0 using the batch procedure. The results are shown in Fig. 3. Quantitative recoveries ($>95\%$) for Co(II), Cd(II), Pb(II), and Pd(II) ions were found in the pH range 4.0–7.0. At $\text{pH} < 2.0$, the adsorption quantity of investigated metal ions was very low, which can be attributed to the protonation of the adsorbent; the more the pH increased, the higher the adsorption quantity obtained. At pH 4.0, it was possible to carry out the determination of Co(II), Cd(II), Pb(II), and Pd(II) simultaneously. So pH 4.0

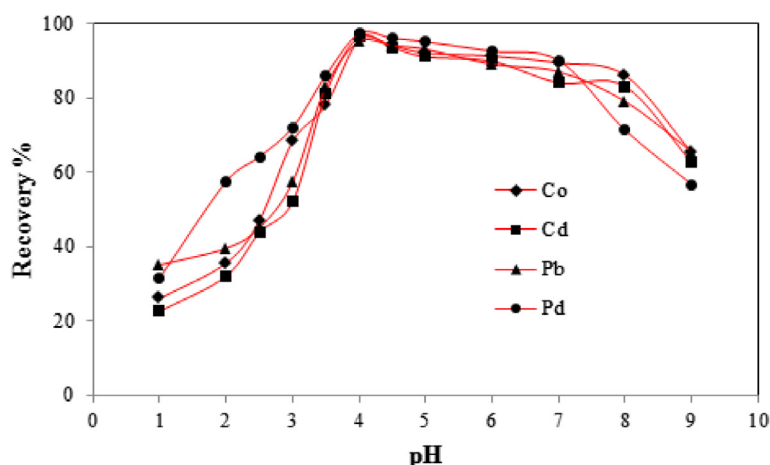


Figure 3 Effect of pH on adsorption of metal ions on MWCNTs-GDH. Other conditions: 250 mg of MWCNTs-GDH and temperature 25°C .

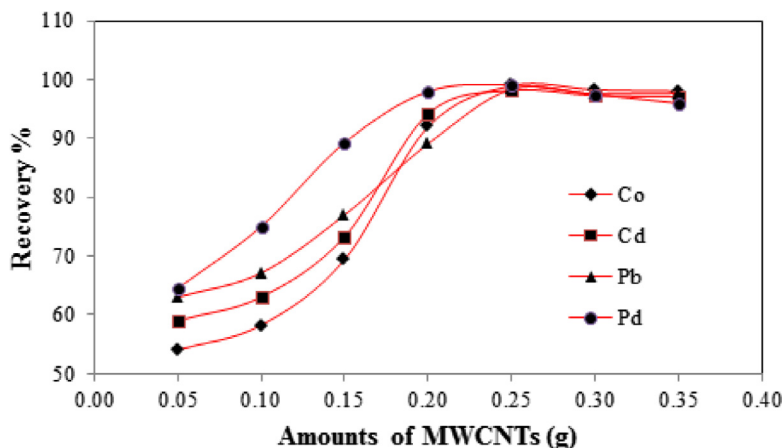


Figure 4 Effect of amount of sorbent on adsorption of metal ions; other conditions: pH 4.0 and temperature 25°C .

was chosen as the optimum pH for further studies and was maintained by using universal aqueous pH buffer solutions.

3.3. Effect of amounts of MWCNTs-GDH

The effect of the amount of MWCNTs-GDH on the adsorption of analytes was investigated at the optimal conditions

that had been determined before. A range of 50–300 mg MWCNTs-GDH was used to find the best recoveries. The results are given in Fig. 4. As expected, increasing the amount of adsorbent led to an increase in the percentage of the analyte adsorbed. MWCNTs-GDH have very high adsorption capacity; for a given concentration of analytes, an appropriate amount of adsorbent is enough and using more is not

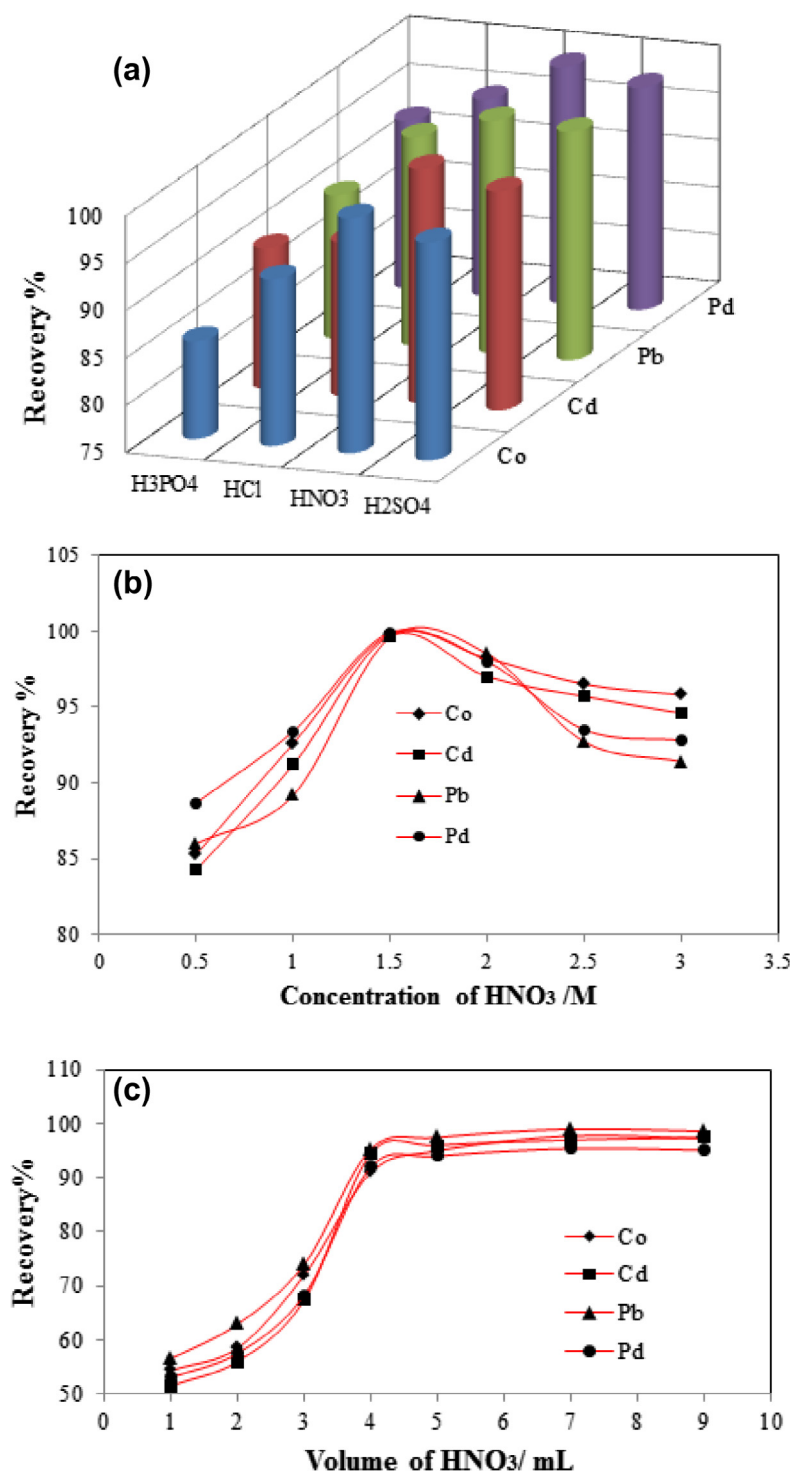


Figure 5 Effect of (a) Type (b) Concentration (c) Volume of the eluent. Other conditions: 250 mg MWCNTs-GDH, pH 4.0, and temperature 25 °C.

necessary. The recovery values for analyte ions were found quantitative for an adsorbent amount of 250 mg. In all further studies, 250 mg MWCNTs-GDH was used.

3.4. Elution conditions

Choosing an appropriate type, volume, and concentration of the eluent used to remove metal ions from the adsorbent are important factors that affected the SPE preconcentration procedure. In this study, 1.5 mol L⁻¹ HNO₃ was used as a general eluent that led to satisfactory results. Meanwhile, other eluents, including 2.0 and 4.0 mol L⁻¹ HNO₃, 2.0 and 4.0 mol L⁻¹ H₃PO₄, and 1.0, 2.0, and 3.0 mol L⁻¹ HCl, were tested, but the recoveries were not remarkable. The elution conditions were also studied by using different concentrations and volumes of 1.5 mol L⁻¹ HNO₃ for the desorption of retained Co(II), Cd(II), Pb(II), and Pd(II) from MWCNTs-GDH. The results are shown in Fig. 5, respectively. The results showed that quantitative recoveries of analyte ions were obtained only with 4.0 mL of 1.5 mol L⁻¹ HNO₃, which was used in further experiments.

3.5. Effect of sample solution volume

The volume of aqueous solution is a critical and important factor in the solid phase extraction of the metal ions to obtain high preconcentration factor. The influence of sample volume on the recovery of Co(II), Cd(II), Pb(II), and Pd(II) ions on modified multiwalled carbon nanotubes was investigated in

Table 3 Analysis of certified reference material.

Analyte	Certified value (μg g ⁻¹)	Measured value (μg g ⁻¹)
Co	0.39 ± 0.04	0.41 ± 0.03
Cd	0.022 ± 0.003	0.021 ± 0.005
Pb	<0.010	0.0092
Pd	326 ± 1.6	344 ± 26

The number of measurements made for each solution was 5.

the range of 100–700 mL. The results are depicted in Fig. 6. The above ions were recovered well up to 400 mL of sample volume. The preconcentration factor for simultaneous preconcentration was calculated by the ratio of the highest sample volume (400 mL) to the lowest eluent volume (4.0 mL) and the preconcentration factor result was 100.

3.6. Adsorption capacities

Adsorption capacity is an important parameter for the evaluation of adsorbent, because it determines how much sorbent is required for quantitative enrichment of the analyte from a given solution (Tunceli and Turker, 2002). In order to evaluate the adsorptive capacity of the modified MWCNTs, a batch method was used. 50 mL of solution containing 5.0 mg of Co(II), Cd(II), Pb(II) and Pd(II) (individually) at pH 4.0 was added to 50.0 mg of sorbent. The mixture was filtered, after shaking for 12 h. 10.0 mL of the supernatant solution was diluted to 100.0 mL and determined by FAAS. The capacity

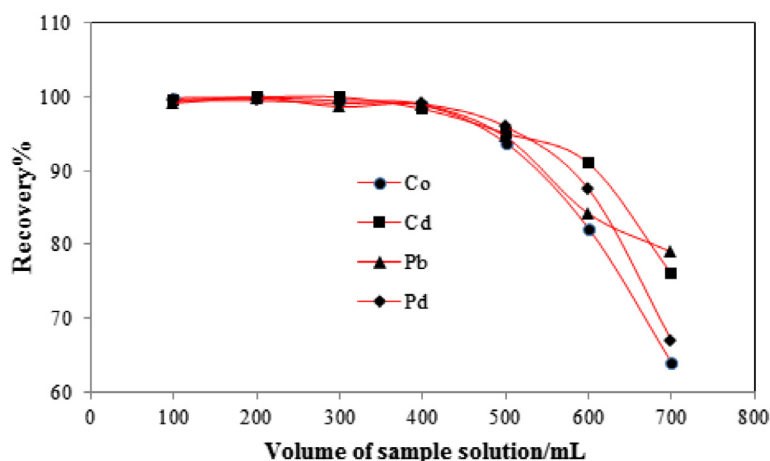


Figure 6 Effect of the sample volume on adsorption of 80 ng mL⁻¹ Co(II), Cd(II), Pb(II), and Pd(II); other conditions: 250 mg MWCNTs-GDH, pH 4.0, and temperature 25 °C.

Table 2 Effects of matrix components on the recovery of the analyte ions. Values in the parentheses are R.S.D. (*N* = 5).

Interference	Tolerance limit (mg)	Recovery (%)			
		Co	Cd	Pb	Pd
Na ⁺	4500	96.9 (1.3)	98.4 (2.8)	97.9 (2.1)	99.1 (1.4)
K ⁺ , Ca ²⁺ , Mg ²⁺	2500	97.0 (2.5)	98.1 (1.2)	96.2 (2.6)	97.4 (1.6)
NO ₃ ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	1500	97.8 (1.7)	96.3 (2.3)	97.1 (1.9)	96.2 (1.4)
Ag ⁺	400	98.1 (1.5)	95.5 (2.9)	96.0 (3.0)	94.9 (2.6)
Ni ²⁺ , Mn ²⁺	200	96.3 (2.7)	96.3 (2.6)	96.7 (2.6)	95.3 (2.4)
Cu ²⁺ , Zn ²⁺ , Hg ²⁺	100	95.5 (2.1)	97.7 (3.0)	94.3 (3.2)	96.1 (2.1)
Al ³⁺ , Fe ³⁺ , Cr ³⁺	50	95.2 (1.9)	95.2 (1.8)	93.6 (2.9)	94.8 (3.1)

Table 4 Application of presented method well water, waste water and soil samples. Values in the parentheses are R.S.D. ($N = 5$).

Analyte	Added ($\mu\text{g L}^{-1}$)	Wastewater ^a		Well water ^b		Soil ^c	
		Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Co	0	85.0 (2.3)	—	12.6 (1.5)	—	107.8 (1.2)	—
	10	94.8 (1.6)	98	22.5 (1.6)	99	118.0 (1.4)	102
Cd	0	55.0 (1.8)	—	16.4 (2.6)	—	112.0 (2.0)	—
	10	65.6 (1.4)	106	26.5 (1.8)	101	122.3 (1.9)	103
Pb	0	121.0 (1.1)	—	18.2 (2.0)	—	98.3 (1.6)	—
	10	131.5 (1.6)	105	28.6 (1.1)	104	108.8 (2.6)	105
Pd	0	76.0 (2.1)	—	37.9 (1.7)	—	87.7 (1.4)	—
	10	85.7 (1.9)	97	47.7 (2.8)	98	97.8 (1.5)	101

^a Wastewater sample was collected from Sarchashmeh of Kerman Industrial State, Iran.

^b Well water sample was collected from husbandry well water, Zarand of Kerman, Iran.

^c Soil sample was collected from part concentrate Sarchashmeh of Kerman factory of Iran.

of sorbent for Co(II), Cd(II), Pb(II), and Pd(II) was found to be 32.5, 27.3, 44.5 and 34.1 mg g^{-1} , respectively. The amounts of sorbed mentioned metal ions were calculated as follows:

$$q_e = (C_0 - C_t) \times V/m \quad (1)$$

where q_e is the amount of metal ions sorbed onto MWCNTs-GDH at equilibrium (mg g^{-1}); C_0 is the initial concentration (mg L^{-1}); C_t is the concentration after a certain period of time (mg L^{-1}); V is the initial solution volume (L); and m is the MWCNTs-GDH mass (g).

3.7. Effects of coexisting ions

The retention of Co(II), Cd(II), Pb(II), and Pd(II) onto MWCNTs-GDH, as it is already mentioned, exhibits a typical electrostatic interaction. Thus, even though MWCNTs-GDH had a high surface area as well as a high volume of pores, the presence of other cationic species still could provoke competition for sorption sites of sorbent. In these experiments, solutions of $20.0 \mu\text{g L}^{-1}$ of Co(II), Cd(II), Pb(II), and Pd(II) containing the added interfering ions, were treated according to the recommended procedure. The tolerance limit was defined as the highest amount of foreign ions that produced an error not greater than $\pm 3\%$ in the determination of investigated analyte ions. The results, summarized in Table 2, clearly show that the proposed method is selective and can be used for various samples for determination of these metal ions without interference.

3.8. Linear ranges, LODs, and precision

Calibration graphs were prepared using a series of 250 mL analyte solutions (initial concentration, $5.0\text{--}150 \text{ ng mL}^{-1}$) pre-concentrated under the optimum conditions. The linear ranges for Co(II), Cd(II), Pb(II), and Pd(II) were $5\text{--}140$, $5\text{--}160$, $5\text{--}160$, and $5\text{--}180 \text{ ng mL}^{-1}$, respectively. The LODs of the method (evaluated as the concentration corresponding to three times the SD of 10 runs of a blank solution) were found to be 0.16, 0.19, 0.17, and 0.12 ng mL^{-1} for Co(II), Cd(II), Pb(II), and Pd(II), respectively. The RSDs of 10 replicate determinations were Co(II) 0.75%, Cd(II) 0.85%, Pb(II) 1.16%; and Pd(II) 1.30% ($C_{\text{Metal ions}} = 100 \text{ ng mL}^{-1}$) which indicated that the method had good precision for the determination of these analytes in sample solutions.

3.9. Application of the method

In order to verify the accuracy of the method, the palladium content of a certified reference material, NIST2556 (used catalyst pellets), was determined. The solid was dissolved as described in the experimental section resulting in a sample solution containing 1.10 mg L^{-1} Pd in 5.0 mol L^{-1} HCl and 2.0 mol L^{-1} HNO_3 . It was necessary to dilute the sample solution due to its high acidity and its considerable metal content.

Working standards (Part Nos. Pb: N9300128; Cd: N9300107) were prepared by serial volume/volume dilution in polypropylene vials ASTM® Type I deionized water acidified with 0.2% nitric acid (HNO_3) was used as the calibration blank and for all dilutions. Thirty percent hydrogen peroxide (H_2O_2) was used for digestion along with nitric acid.

In order to assess the accuracy and validity of the developed procedure, the method was applied for separation and determination of cobalt in spinach leaves (NIST 1570a).

The analytical data are summarized in Table 3. The obtained data are in good agreement with certified values that was confirmed by using Student's t -test (Konieczka and Namieśnik, 2009). The precision of nickel and cobalt determination by the presented method can be regarded as acceptable for this application. Substantial agreement between the mean results and the certified values was obtained for five replicate measurements with discrepancies of less than 9% for Pd, 8% for Pb, 5% for Cd and 7% for Co.

The proposed procedure has been applied to the determination of trace Co(II), Cd(II), Pb(II), and Pd(II) in soil, well water, and wastewater in order to investigate the applicability of the method for real samples. The results are shown in Table 4. The recovery of tested samples was acceptable; thus, we can recommend the presented method for the preconcentration of metal ions in different real samples.

4. Conclusion

This work has demonstrated the feasibility of the developed solid phase extraction method based on adsorption of Co(II), Cd(II), Pb(II), and Pd(II) ions on MWCNTs-GDH prior to their atomic absorption spectrometric determination. These sorbents are simple and cost-effective, and can be used several

times without a marked loss in sorption capacity. This is the key factor for the fact that whether a novel but expensive sorbent can be accepted by the field or not. The developed method is simple, rapid, precise, accurate and reliable offering a higher preconcentration factor and adsorption capacity for the above metal ions rather than other sorbents. Table 1 compares the proposed method with those reported previously for the determination of Co(II), Cd(II), Pb(II), and Pd(II) ions after preconcentration procedure (Afzali and Mostafavi, 2008; Zang et al., 2009; Shamspur, 2009; Tuzen et al., 2008). The results show that the detection limits of the measurement were remarkably better in addition to the fact that preconcentration factor is relatively higher than the mentioned methods.

References

- Abdel Salam, M., Burk, R., 2008. *Anal. Bioanal. Chem.* 390, 2159–2170.
- Adams, C., Nie, Y., Qiang, Z., Zhang, H., 2009. *J. Chromatogr. A* 1216, 7071–7080.
- Afzali, D., Mostafavi, A., 2008. *Anal. Sci.* 24, 1135–1139.
- Al-Degs, Y.S., Al-Ghouti, M.A., El-Sheikh, A.H., 2009. *J. Hazard. Mater.* 169, 128–137.
- Al-Degs, Y.S., Al-Ghouti, M.A., Hemmateenejad, B., El-Sheikh, A.H., Walker, G.M., 2008. *Talanta* 75, 904–915.
- Behbahani, M., Bide, Y., Salarian, M., Niknezhad, M., Bagheri, S., Bagheri, A., Nabid, M.R., 2014a. *Food Chem.* 158, 14–19.
- Behbahani, M., Sadeghi Abandansari, H., Salarian, M., Babapour, M., Bagheri, A., Nabid, M.R., 2014b. *Microchim. Acta* 181, 129–137.
- Chai, X., Chang, X., Hu, Z., He, Q., Li, Z., Tu, Z., 2010. *Talanta* 82, 1791–1796.
- Chen, S., Liu, C., Lu, D., Wang, Z., Wang, M., Zhu, L., 2009. *J. Hazard. Mater.* 170, 247–251.
- Clark, A., 1974. *The Chemisorptive Bond*. Academic Press, New York and London.
- Dean, J.R., 1998. *Extraction Methods for Environmental Analysis*. Wiley, New York.
- Ding, Q., Du, D., Liang, P., Zhao, E., 2008. *Spectrochim. Acta B* 63, 714–717.
- Ding, Y., Xiao, J., Zhou, Q., 2006. *Anal. Bioanal. Chem.* 385, 1520–1525.
- Fang, G., Min, G., Wang, S., Zhao, P., 2007. *J. Chromatogr. A* 1, 165–166.
- Fritz, J.S., 1999. *Analytical Solid-Phase Extraction*. Wiley-VCH, New York.
- Ghaedi, M., Ahmadi, F., Soylak, M., 2007. *J. Hazard. Mater.* 147, 226–231.
- Ghaedi, M., Khanjari, N., Kianfar, A.H., Mirsadeghi, A.S., Pourfarokhi, A., Shokrollahi, A., Soylak, M.J., 2009. *Hazard. Mater.* 162, 1408–1414.
- Grobert, N., 2007. *Mater. Today* 10, 28–35.
- Hajipour, A., Zahmatkesh, S., Ruoho, A.E., 2007. *E. Polymers*, No. 088.
- Han, Y., Li, Y., Si, W., Wei, D., Yao, Z., Zheng, X., Du, B., Wei, Q., 2011. *Spectrochim. Acta A* 79, 1546–1551.
- Huang, H., Ji, Y., Jiang, X., Liu, X., Wang, C., Xu, Z., Zhang, H., 2009. *Chromatographia* 70, 753–757.
- Iijima, S., Ichihashi, T., 1993. *Nature* 363, 603–605.
- Konieczka, P., Namieśnik, J., 2009. *Quality Assurance and Quality Control in the Analytical Chemical Laboratory: A Practical Approach*. CRC Press, Boston, MA, USA.
- Mansor, N.B.A., Tessonier, J.P., Rinaldi, A., Reiche, S., Kutty, M.G., 2012. *Sains Malays.* 41, 603–609.
- Mashhadizadeh, M.H., Karami, Z., 2011. *J. Hazard. Mater.* 190, 1023–1029.
- Mashhadizadeh, M.H., Shamspur, T., Sheikhshoae, I., 2003. *J. Anal. At. Spectrom.* 18, 1407–1410.
- Nabid, M.R., Sedghi, R., Bagheri, A., Behbahani, M., Taghizadeh, M., Abdi Oskooie, H., Heravi, M.M., 2012. *J. Hazard. Mater.* 203–204, 93–100.
- Nabid, M.R., Sedghi, R., Hajimirza, R., Oskooie, H.A., Heravi, M.M., 2011. *Microchim. Acta* 175 (3–4), 315–322.
- Parinejad, M., Nasira, H., Yafian, M.R., 2008. *Can. J. Anal. Sci. Spectrosc.* 53, 163–170.
- Poole, C.F., 2003. *Trends Anal. Chem.* 22, 362–373.
- Pretsch, E., Buhlmann, P., Badertscher, M., 2009. *Structure Determination of Organic Compounds – Tables of Spectral Data*, fourth ed. Springer, pp. 269–335.
- Shamspur, T., 2009. *J. Hazard. Mater.* 168, 1548–1553.
- Soylak, M., Saygi, K.O., Tuzen, M., 2008. *J. Hazard. Mater.* 99, 1563–1570.
- Tan, X., Fang, M., Chen, C., Yu, S., Wang, X., 2008. *Carbon* 46, 1741–1750.
- Tavallali, H., Deilamy-Rad, G., Peykarimah, P., 2013. *J. Environ. Monitor.* 185, 7723–7738.
- Tunceli, A., Turker, R., 2002. *Talanta* 57, 1199–1204.
- Tuzen, M., Saygi, K.O., Soylak, M., 2008. *J. Hazard. Mater.* 152, 632–639.
- Vaghetti, J.C.P., Lima, E.C., Royer, B., da Cunha, B.M., Cardoso, N.F., Brasil, J.L., Dias, S.L.P., 2009. *J. Hazard. Mater.* 162, 270–280.
- Wang, Y., Duan, Y., Yang, L., Zhao, C., Shen, X., Zhang, M., Zhuo, Y., Chen, C., 2009. *Fuel Process. Technol.* 90, 643–651.
- Yang, B.W., Fan, Z.F., 2008. *At. Spectrosc.* 29, 193–197.
- Zhang, L., Li, Z., Du, X., Li, R., Chang, X., 2012. *Spectrochim. Acta A* 86, 443–448.
- Zang, Z., Hu, Z., Li, Z., He, Q., Chang, X., 2009. *J. Hazard. Mater.* 172, 958–963.